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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

Date: 12-MAR-2009

SUBJECT: **Malathion.** Magnitude of the Residue of Malathion, Malaoxon and Desmethyl Malathion in/on Stored Wheat Grain, Rice and Processed Commodities.

PC Code: 057701
Decision No.: NA
Petition No.: NA
Risk Assessment Type: Single Chemical Aggregate
TXR No.: NA
MRID No.: 47506701

DP Barcode: 292680; 361372
Registration No.: NA
Regulatory Action: Field Trial Study
Case No.: 0248

CAS No.: 121-75-5
40 CFR: 180.111

FROM: Sheila Piper, Chemist/Risk Assessor Sheila Piper
Risk Assessment Branch VI
Health Effects Division (7509P)

THROUGH: Felecia Fort, Chief Felecia Fort
Risk Assessment Branch VI
Health Effects Division (7509P)
Office of Pesticide Programs

TO: Eric Miederhoff, Chemical Review Manager
Reregistration Branch III
Special Review and Reregistration Division (7508P)

Executive Summary

Malathion is a non-systemic, wide spectrum organophosphorus insecticide. It is used in the agricultural production of a wide variety of food/feed crops to control insects such as aphids, leafhoppers, and Japanese beetles. Malathion is also used in the Cotton Boll Weevil Eradication Program, Fruit Fly (Medfly) Control Program, and mosquito-borne disease control. It is also available to the home gardener for outdoor residential uses which include vegetable gardens, home orchards and ornamentals.

Tolerances are established for residues of malathion *per se* (O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate) in/on various plant commodities [40 CFR

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180.111]. A tolerance of 8 ppm has been established for residues of malathion *per se* in/on wheat grain. No tolerance for aspirated grain fractions or any processed wheat grain commodity has been established. The qualitative nature of malathion residues in plants is adequately understood. The residues of concern are malathion and malaoxon.

In response to the Malathion Reregistration Eligiblility Decision (RED) Document the registrant was required to propose appropriate tolerances for malathion residues in bran, flour, middlings, and shorts processed from wheat grain treated postharvest with malathion. The data from this study will be translated to the processed commodities of stored barley, oat and rye grain (D216397, 05/26/1998, M. Xue). This data are evaluated in this document for adequacy in fulfilling residue chemistry requirements.

860.1500 & 860.1520 Crop Field Trial and Processed Food/Feed
47506701.der [S.Piper, 01/15/2009]

Cheminova has submitted a magnitude of residue study on stored wheat grain from storage bins that were treated with Malathion 57EC and Big 6® Grain Protector to determine the magnitude of the residue of malathion, malaoxon, and desmethyl malathion in the whole grain and in processed commodities produced from the grain (7506707der, S. Piper, 01/15/09). The empty storage bins were treated with a malathion emulsifiable concentrate formulation containing 57% malathion prior to loading of the grain, and the grain was subsequently treated three times with a malathion dust formulation. Four storage bins (~40 bushels of wheat grain (~2400 lb) were conducted in Carlyle, IL during the 2007 growing season. A total of 74 wheat grain; 2 aspirated grain fraction; and 24 wheat processed commodity samples (2 each of pre-processing grain, cleaned grain, bran, germ, straight flour, middlings, shorts, whole meal flour, 550 flour, vital gluten whole meal bread, and white bread) were analyzed. Each bin was 4 feet high by 4 feet long by 3.5 feet wide (56 ft^3) and could hold up to ~40 bushels of wheat grain (~2400 lb). Applications 1, 2, 3 were accomplished on the same day (see Table 1). Wheat grain samples were analyzed between 20 and 104 days after collection in the field. The processed commodity samples were analyzed between 15 and 31 days after being processed. Previously submitted storage stability data which indicated that residues of malathion and malaoxon are relatively stable under frozen storage conditions for 12 months in/on wheat straw, bran, flour, middlings and shorts (D223392, SEP-23-1997, W.Smith).

TABLE 1. Study Use Pattern.

Application No.	Test Substance Formulation	Target Application Rate	Application Timing
1	Malathion 57 EC	8 pints/25 gallons water Apply 3.0±0.15 gal/1000ft^2 (0.6 lb ai/1000ft^2) (293 g ai/100m^2)	Thoroughly spray the floor and walls of bins prior to filling the bins with wheat
2	Big 6® Grain Protector (6% Dust)	10.4 lb product/1000 bushels (0.62 lb ai/1000 bushels) (10.3 g ai/metric ton)	Apply to the grain in the wagon, mix into the grain, then transfer into the storage bin
3		5.2 lb product/1000ft^2 (0.31 lb ai/1000ft^2) (151 g ai/100m^2)	Apply to the top of the grain in the storage bin immediately after filling

4		5.2 lb product/1000ft^2 (0.31 lb ai/1000ft^2) (151 g ai/100m^2)	Apply to the top of the grain in the storage bin 60 days after filling

The malathion (13.6 ppm) and malaoxon (<0.01 ppm) residues were found in the treated grain samples collected after 10 days. Malathion (15.1 ppm) and malaoxon (<0.01 ppm) residues were also collected 29 days after the last application. In the processing phase, the treated grain sample collected immediately prior to processing contained 15.0 ppm of malathion and <LOQ malaoxon. The highest residues found in the aspirated grain fraction sample contained 2690 ppm of malathion and 0.98 ppm of malaoxon (See tables 2 and 3).

TABLE 2. Wheat Grain Sample Residues

Sample Event	Malathion	Malaoxon	Combined
	Maximum (ppm)		
Post-application #2/Pre-application #3	9.28	<0.01	9.28
Post-application #3	12.4	<0.01	12.4
Pre-application #4	9.76	<0.01	9.76
Post-application #4	12.3	<0.01	12.3
10 days Post-application #4	13.6	<0.01	13.6
29 days Post-application #4	15.1	<0.01	15.1

TABLE 3. Processed Commodity Sample Residues

Field Sample	Trt ID	Sample Type	Malathion ppm	Malaoxon ppm	Combined ppm
Processing Bulk Sample	TRT#2	Pre-Processing Grain	15.0	<0.01 (0.0046)	15.01
		Aspirated Grain Fractions	2690	0.984	2691
		Cleaned Grain	11.9	<0.01 (0.0044)	11.9
		Bran	8.08	<0.01 (0.0016)	8.09
		Germ	14.0	<0.01 (0.0039)	14.0
		Straight Flour	1.34	ND	1.34
		Middlings	3.26	<0.01 (0.0010)	3.27
		Shorts	9.04	<0.01 (0.00136)	9.05
		Whole Meal Flour	11.2	<0.01 (0.0045)	11.21
		550 Flour	2.14	ND	2.14
		Vital Gluten	0.0178	ND	0.0178
		Whole Meal Bread	1.84	<0.01 (0.0010)	1.85

		White Bread	0.295	<0.01 (0.0004)	0.305

Regulatory Conclusions

The submitted study satisfies OPPTS 860.1500 (crop field trials) and 860.1520 (processed food/feed) for postharvest treated wheat grain. Combined residues of malathion and malaoxon in/on postharvest field wheat grain is 15 ppm. Combined residues of malathion and malaoxon in wheat grain concentrated in aspirated grain fraction (179x) is 2691 ppm. The Agency recommended establishing tolerances for malathion and malaoxon in the processed commodities, bran (8 ppm), whole meal flour (11 ppm), middlings (4 ppm), germ (14 ppm) and shorts (9 ppm) and has reassessed the tolerance of wheat grain postharvest to 15 ppm. The data supports the maximum rate of four applications at 5.2 lb product/1000 ft^2. The label should be amended to reflect this application. Also, Cheminova has requested post-harvest rice use; therefore, malathion residue data on stored wheat grain are translatable to stored grain of rice.

References

1. DP Barcode: D330680
   Subject: Malathion Reregistration Eligiblity Decision (RED)
   From: S.Piper
   To: T.Moriarty
   Dated: 07/31/2006
   MRID(s): NA

2. DP Barcode: D216397
   Subject: Malathion and Malaoxon in/on Stored Grains and Processed Commodities
   From: M. Xue
   To: D. Locke
   Dated: 05/26/1998
   MRID(s): 43661401; 43666801

3. DP Barcode: D187727
   Subject: Malathion: Protocol for Stored Grain and Grain Dust Residue Studies and Corn Processing Study
   From: D.McNeilly
   To: P.Perreault
   Dated: 04/14/1993
   MRID(s): NA

RDI: S.Piper, RAB6 (03/11/09): Potomac Yard 1: 703-308-2717; 47506707.der.wpd

Malathion/ 057701/Cheminova
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial/ Processed – Stored Wheat Grain and Processed Commodities

Primary Evaluator Sheila Piper Date: 03/121/09
Sheila Piper, Chemist
Risk Assessment Branch (RAB VI)
Health Effects Division (HED, 7509P)

Approved by Felecia Fort Date: 03/12/09
Felecia Fort, Chief
RAB VI/HED 7509P

STUDY REPORTS:

MRID 47506701. Willard, T.R. (2008). Magnitude of the Residue of Malathion, Malaoxon, and Desmethyl Malathion in Stored Wheat Grain and Processed Commodites. Study No.AA070707. 679 pages.

EXECUTIVE SUMMARY:

Cheminova has submitted magnitude of residue study on stored wheat grain from storage bins that were treated with Malathion 57EC and Big 6® Grain Protector to determine the magnitude of the residue of malathion, malaoxon, and desmethyl malathion in the whole grain and in processed commodities produced from the grain. The empty storage bins were treated with a malathion emulsifiable concentrate formulation containing 57% malathion prior to loading of the grain, and the grain was subsequently treated three times with a malathion dust formulation. Four storage bins (~40 bushels of wheat grain (~2400 lb) were conducted in Carlyle, IL during the 2007 growing season. A total of 74 wheat grain; 2 aspirated grain fraction; and 24 wheat processed commodity samples (2 each of pre-processing grain, cleaned grain, bran, germ, straight flour, middlings, shorts, whole meal flour, 550 flour, vital gluten whole meal bread, and white bread) were analyzed.

Stability data for malathion and malaoxon were not generated as part of this study because adequate data have already been submitted. Wheat grain samples were analyzed between 20 and 104 days after collection in the field. The processed commodity samples were analyzed between 15 and 31 days after being processed. Previously submitted storage stability data which indicated that residues of malathion and malaoxon are relatively stable under frozen storage condition for 12 months in/on wheat straw, bran, flour, middlings and shorts (W.Smith D223392, 9/23/1997). Analyses to determine the stability of desmethyl malathion residues in wheat grain were held in frozen storage (-20±5°C). These data indicate that the desmethyl malathion residues were not stable in homogenized wheat grain stored under frozen conditions for 104 days, the longest storage period experienced by the whole grain samples collected in this study. Therefore, a separate study is being initated that will investigate the stability of desmethyl malathion residues in wheat grain stored for periods of 44 days and less.

After storage, the samples were analyzed for residues of malathion, malaoxon, and desmethyl malathion in the whole grain and in processed commodities produced from the grain (using HPLC employing tandem mass spectrometric (MS/MS) detection Project No. Ml07-1410-CVA). The method was adequately validated in conjunction with the analysis of field trial samples. For this method, malathion and its metabolites (malaoxon and desmethyl malathion) were extracted from the sample matrix by blending with acetonitrile. An aliquot of the extract was filtered through a PTFE filter, evaporated to dryness, and reconstituted in HPLC methanol: 0.1% formic acid in HPLC grade water (50:50,v/v) for HPLC analysis. The limit of quantitation (LOQ) for malathion, malaoxon, and desmethyl malathion residues in all matrices was 0.01 ppm except for malathion in aspirated grain fractions, which was 0.1 ppm.

The malathion (13.6 ppm), desmethyl malathion (0.698 ppm) and malaoxon (<LOQ) residues were found in the treated grain samples collected after 10 days. Malathion (15.1 ppm), desmethyl malathion (0.669 ppm) and malaoxon (<LOQ) residues were also collected 29 days after the last application. In the processing phase, the treated grain sample collected immediately prior to processing contained 15.0 ppm of malathion, <LOQ malaoxon, and 0.61 ppm of desmethyl malathion. The highest residues found in the aspirated grain fraction sample contained 2690 ppm of malathion, 0.98 ppm of malaoxon and 502 ppm of desmethyl malathion.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, D292680.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Malathion is a non-systemic, wide spectrum organophosphorus (OP) insecticide. It is used in the agricultural production of a wide variety of food/feed crops to control insects such as aphids, leafhoppers, and Japanese beetles. Malathion is also used in the cotton boll weevil, fruit fly, and mormon cricket eradication programs and as a general wide-area treatment for mosquito-borne disease control (adulticide). It is also available to the home gardener for outdoor residential uses which include vegetable gardens, home orchards, ornamentals and lawns. The nomenclature and physicochemical properties of malathion and malaoxon are shown in Tables A.1 and A.2.

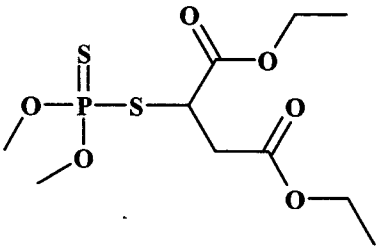
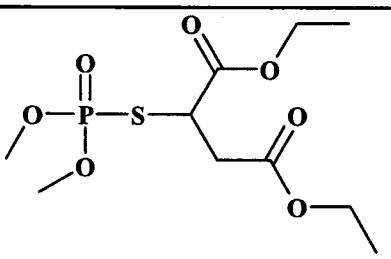
TABLE A.1. Malathion and Malaoxon Nomenclature.	
Compound	Chemical Structure
	
Common name	Malathion
Company experimental name	
IUPAC name	Diethyl (dimethoxythiophosphorylthio)succinate
CAS name	O,O-dimethyl phosphorodithioate of diethyl mercaptosuccinate
CAS #	121-75-5
End-use product/(EP)	Technical (91-95% ai), dust (1-10% ai), emulsifiable concentrate (3-82% ai), ready-to-use (1.5-95% ai), pressurized liquid (0.5-3% ai), and wettable powder (6-50% ai)
	
Common name	Malaoxon
Company experimental name	
IUPAC name	2-(dimethoxyphosphorylthio)butanedioic acid diethyl ester
CAS name	Butanedioic acid, [(dimethoxyphosphinyl)-thio]-diethylester]
CAS #	1634-78-2
End-use product/(EP)	Not Registered

TABLE A.2 Physicochemical Properties of Malathion		
Parameter	Value	Reference
Molecular Weight	330.4	Product Chemistry Chapter (W. Smith, June 2, 1999)
Boiling point/range	156-157°C	Product Chemistry Chapter (W. Smith, June 2, 1999)
Melting point	2.8°C	SRC PhysProp Database
Density (25°C)	1.2	SRC PhysProp Database
Water solubility (25°C)	145 ppm	Product Chemistry Chapter (W. Smith, June 2, 1999)
Solvent solubility (temperature not specified)	readily soluble in most alcohols, esters, aromatic solvents, and ketones, and is only slightly soluble in aliphatic hydrocarbons	Product Chemistry Chapter (W. Smith, June 2, 1999)
Vapor pressure (30°C)	0.00004 mmHg	Product Chemistry Chapter (W. Smith, June 2, 1999)
Octanol/water partition coefficient, $\log K_{ow}$ (25°C)	2.36	SRC PhysProp Database
Half Life	Aerobic soil T½ = 3 days (used for EEC modeling)	
TABLE A.2 Physicochemical Properties of Malaoxon		
Parameter	Value	Reference
Molecular Weight	314.29	Chemical Abstracts
Boiling Point	114°C	
Melting point/range	<20°C	
Water solubility (22°C)	0.5-1.0 g/100 mL	
Vapor pressure (10-50°C)	2.45E-06 to 3.2E-04 torr	
Half Life	Aerobic soil T½ = 21 days (used for EEC modeling)	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Four storage bins were treated at Alvey Agricultural Research, Inc., in Carlyle, IL. Wheat (*Triticum aestivum*, variety Arise 767) was obtained from a local source known not to have been treated with malathion products during its growth or storage. Each bin was 4 feet high by 4 feet long by 3.5 feet wide (56 ft^3) and could hold up to ~40 bushels of wheat grain (~2400 lb). Applications 1, 2, 3 were accomplished on the same day (see Table B.1.1)

TABLE B.1.1 Study Use Pattern.

Application No.	Test Substance Formulation	Target Application Rate	Application Timing
1	Malathion 57 EC	8 pints/25 gallons water Apply 3.0±0.15 gal/1000ft^2 (0.6 lb ai/1000ft^2) (293 g ai/100m^2)	Thoroughly spray the floor and walls of bins prior to filling the bins with wheat
2	Big 6® Grain Protector (6% Dust)	10.4 lb product/1000 bushels (0.62 lb ai/1000 bushels) (10.3 g ai/metric ton)	Apply to the grain in the wagon, mix into the grain, then transfer into the storage bin
3		5.2 lb product/1000ft^2 (0.31 lb ai/1000ft^2) (151 g ai/100m^2)	Apply to the top of the grain in the storage bin immediately after filling
4		5.2 lb product/1000ft^2 (0.31 lb ai/1000ft^2) (151 g ai/100m^2)	Apply to the top of the grain in the storage bin 60 days after filling

Spray Application of Malathion 57 EC (Application #1)
For the spray application of malathion 57 EC a CO_2-pressurized sprayer was used to thoroughly treat the floor and walls in the three treated storage bins (74 ft^2/bin). The mixture was applied at 30 psi to deliver 3.0 gallons of mixture/1000 ft^2 of surface area which equal to 0.6 lb ai/1000 ft^2 (293 g ai/100m^2).

Big 6® Grain Protector (6% Dust) Bin Loading Application (Application #2)
Wheat grain was weighed out so that each bin contained 2000± 100 lbs (31.7 to 35.0 bushels of grain). The grain of each bin was held in a gravity-feed wagon. A pre-weighed amount of the Big 6® Grain Protector was applied to the surface of the grain in the wagon based on the bushels (60 lbs/bushel) of wheat in the wagon and the application rate 10.4 lb products/1000 bushels (0.62 lb ai/1000) bushels; 10.3 g ai/metric ton). The test substance was thoroughly incorporated into the grain using a shovel and augured into the storage bin. The auguring process mixed the test substance into the grain as it moved into the storage bin.

Big 6® Grain Protector (6% Dust) Bin-Top Application (Application #3)
After loading, grain in the storage bin was leveled off. Based on the 14ft^2 surface area a pre-weighed amount of the Big 6® Grain Protector was applied to the surface of the grain in the bin at the application rate of 5.2 lb product/1000 ft^2 (0.31 lb ai/1000ft^2; 151 g ai/100 m^2). The test substance was thoroughly incorporated into the top six inches of the grain and covered.

Big 6® Grain Protector (6% Dust) Bin-Top Application (Application #4)
At 60 days after application #3, the treated bins were opened and Big 6® Grain Protector (6% dust) bin-top application was repeated using the same procedures as described for application #3. The bins were covered until opened to collect samples and take temperature and grain moisture measurements.

The RAC grain samples were collected using a partitioned grain probe capable of collecting grain from various depths within the bin. At each treated bin sampling event, a total of 4 RAC grain samples (1kg) were collected from each bin: A composite (I) was collected from which a primary and a reserve sub-sample was collected; and a second independently-collected, composite sample (II) was collected from which a primary and a reserve sub-sample was collected (see Table B.1.2). When the untreated control bin was scheduled to be sample it was sampled first and covered before any activity in the treated bins.

A composite sample was comprised of at least 12 grain probe samples. The surface area of the bin was divided into four quadrants and three probe samples were collected from each quadrant (near the bin wall, near the center of the bin, and approximately mid-way between the bin wall and center). The probe samples were composited onto a clean plastic sheet. The primary and reserve RAC sample were taken from this composite. The process was repeated to produce the second, independently-collected, composite sample (II) from which the primary and reserve sub-sample were collected.

TABLE B.1.2 Sample Collection.

Treatment ID[1]	Sampling Event	Number and Types of Samples
UTC-TRT#1	Prior to any application	1 wheat grain RAC sample
TRT#2	After bin filling application (Application #2) but prior to the bin top application (Application #3)	4 wheat grain RAC sample from each treated bin
TRT#2	After bin top application (Application #3)	4 wheat grain RAC sample from each treated bin
TRT#2	Immediately prior to the 60-day bin top application (Application #4)	4 wheat grain RAC sample from each treated bin
TRT#2	Immediately after to the 60-day bin top application (Application #4)	4 wheat grain RAC sample from each treated bin
TRT#2	10 days after the 60-day bin top application (Application #4)	4 wheat grain RAC sample from each treated bin
UTC-TRT#1	29 days after the 60-day bin top application (Application #4)	1 wheat grain RAC sample 1 wheat grain bulk sample
TRT#2	29 days after the 60-day bin top application (Application #4)	4 wheat grain RAC sample from each treated bin 1 wheat grain bulk sample that is a composite sample from the 3 treated bins

[1] UTC-untreated control

B.2. Sample Handling and Preparation

Wheat grain samples were analyzed between 20 and 104 days after collection in the field. Grain samples collected prior to and following the 4th application and at 10 and 29 days after the 4th application were stored for a maximum of 44 days prior to extraction. The RAC grain samples were placed into labeled sample bags and kept in freezer storage (-20±5°C) until shipment to the

analytical laboratory via FedEx with dry ice. The processed commodity samples were analyzed between 15 and 31 days after being processed by the processing facility. The bulk grain samples were received at GLP Technologies, Navasota, TX a day after collection and were placed into freezer storage until processing. The processed commodity samples were stored for 31 days or less prior to extraction. A separate study will investigate the stability of desmethyl malathion residues in wheat grain stored for periods of 44 days and less (available study showed that desmethyl malathion residues were not stable in homogenized wheat grain (19% recovery) stored under frozen conditions for a period of 104 days). Morse Laboratories, Inc., Sacramento, CA conducted and reported the analytical phase of this study.

B.3. Analytical Methodology

Samples were analyzed using "Analytical Method and Validation for the Determination of Malathion, Malaoxon, and Desmethyl-Malathion in Rape Seed, Plants and Pods" (3/13/2006) and Morse Labs modifications to the method (2/20/2008).

Malathion and its metabolites (malaoxon and desmethyl malathion) were extracted from the sample matrix by blending with acetonitrile. An aliquot of the extract was filtered through a PTFE filter, evaporated to dryness, and reconstituted in HPLC methanol: 0.1% formic acid in HPLC grade water (50:50v/v) for HPLC analysis. Determination and quantitation of the analytes were conducted using HPLC employing tandem mass spectrometric (MS/MS) detection. The LOQ for malathion, malaoxon, and desmethyl malathion residues in all matrices was 0.01 ppm except for malathion in aspirated grain fractions, which was 0.1 ppm.

C. RESULTS AND DISCUSSION

The longest storage interval (104 days) was only applicable to the grain samples collected during the first applications. Grain samples collected prior to and following the 4th application and at 10 and 29 days after the 4th application were stored for a maximum of 44 days prior to extraction. In addition pre-processing grain was stored for 44 days and the processed commodity samples were stored for 31 days or less prior to extraction (see Table C.2). Based on previously submitted storage stability data which indicated that residues of malathion are stable for 12 months, HED concludes that the storage intervals have been validated. Analyses to determine the stability of desmethyl malathion residues in wheat grain held in frozen storage (-20±5°C). These data indicate that the desmethyl malathion residues were not stable in homogenized wheat grain stored under frozen conditions for 104 days, the longest storage period experienced by the whole grain samples collected in this study. Therefore, a separate study is being initated that will investigate the stability of desmethyl malathion residues in wheat grain stored for periods of 44 days and less.

After storage, the samples were analyzed for residues of malathion, malaoxon, and desmethyl malathion in the whole grain and in processed commodities produced from the grain (using HPLC employing tandem mass spectrometric (MS/MS) detection Project No. Ml07-1410-CVA.

The method was adequately validated in conjunction with the analysis of field trial samples. The average method validation recovery was 102% for malathion, 104% for malaoxon and 100% for desmethyl malathion in wheat grain. The average concurrent recovery was 100% for malathion, 98% for malaoxon and 84% for desmethyl malathion in wheat grain (see Table C.1). The LOQ for malathion, malaoxon, and desmethyl malathion residues in all matrices was 0.01 ppm except for malathion in aspirated grain fractions, which was 0.1 ppm.

The maximum malathion residues (13.6 ppm) and desmethyl malathion (0.70 ppm) were found in the treated grain samples collected at 10 days and 29 days after the last application (15.1 ppm for malathion and 0.67 ppm for desmethyl malathion). Malaoxon was not found at levels >LOQ in any wheat grain samples (see Table C.3). In the processing phase, the treated grain sample collected immediately prior to processing contained 15.0 ppm of malathion, <LOQ malaoxon, and 0.61 ppm of desmethyl malathion. The highest residues found in the aspirated grain fraction (AGF) sample contained 2690 ppm of malathion, 0.98 ppm of malaoxon and 502 ppm of desmethyl malathion.

Malathion residues in treated grain used to generate aspirated grain fraction were 15.0 ppm and concentrated to 2690 ppm, a concentration factor of 179 (see Table C.4). None of the analytes increased in concentration into any of the processed commodities (see Table C.5). The untreated grain sample contained 0.3 lb/723 lb of grain (0.04% AGF), while treated sample contained 0.5 lb/711 lb of grain (0.07%). The ash content of AGF from treated and control grain was 6.9 and 7.1%, respectively. The size distribution of AGF from control and treated grain was 82 and 87% respectively, of the AGF was in the fraction <425 microns.

TABLE C.1. Summary of Concurrent Recoveries of Malathion from Wheat Grain

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev (%)
Method Validation					
Grain	Malathion	0.01	7	100, 108, 94, 102, 101, 99, 97	100 ± 4
		0.1	5	105, 101, 100, 101, 103	102 ± 2
		1.0	5	106, 99, 104, 102, 104	103 ± 3
		TOTAL	**17**	**94- 108**	**102 ± 3**
	Malaoxon	0.01	7	102, 109, 106, 103, 103, 108, 111	106 ± 4
		0.1	5	104, 102, 103, 100, 104	103 ± 2
		1.0	5	104, 103, 107, 102, 104	104 ± 2
		TOTAL	**17**	**100- 111**	**104 ± 3**
	Demethyl malathion	0.01	7	78, 92, 77, 91, 100, 95, 101	91 ± 10
		0.1	5	107, 110, 101, 110, 111	108 ± 4
		1.0	5	111, 104, 101, 108, 98	104 ± 5
		TOTAL	**17**	**77- 111**	**100 ± 10**
Aspirated grain fractions	Malathion	0.01	7	105, 96, 100, 96, 96, 101, 102	99 ± 4
		0.1	5	98, 112, 104, 102, 106	104 ± 5
		10	5	106, 108, 96, 97, 104	102 ± 5
		TOTAL	**17**	**96- 112**	**102 ± 5**
	Malaoxon	0.01	7	101, 107, 103, 103, 105, 101, 95	102 ± 4
		0.1	5	96, 110, 102, 97, 104	102 ± 6

TABLE C.1. Summary of Concurrent Recoveries of Malathion from Wheat Grain					
Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev (%)
		1.0	5	106, 106, 96, 110, 114	106 ± 7
		TOTAL	**17**	**95- 114**	**103 ± 5**
	Demethyl malathion	0.01	7	104, 97, 114, 98, 74, 82, 103	96 ± 14
		0.1	5	108, 123, 117, 91, 109	110± 12
		1.0	5	100, 94, 82, 101, 108	97 ± 10
		TOTAL	**17**	**74- 123**	**100 ± 13**
Concurrent Recovery					
Grain	Malathion	0.01	4	94, 83, 110, 100	97± 11
		0.1	2	99, 97	98
		1.0	2	94, 99	96
		16.0	1	104	104
		TOTAL	**9**	**83- 110**	**98 ± 8**
	Malaoxon	0.01	4	100, 99, 106, 96	100± 11
		0.1	2	101, 102	102
		1.0	2	101, 96	98
		TOTAL	**8**	**96- 106**	**100 ± 3**
	Demethyl malaoxon	0.01	3	93, 74, 88	85± 10
		0.1	2	79, 79	79
		1.0	2	92, 85	88
		TOTAL	**7**	**74- 93**	**84 ± 7**
Aspirated grain fractions	Malathion	0.1	1	106	106
		2500	1	94	94
		3000	1	102	102
		TOTAL	**3**	**94- 106**	**101 ± 6**
	Malaoxon	0.01	1	96	96
		1.0	1	98	98
		TOTAL	**2**	**96- 98**	**1097**
	Desmethyl malathion	0.01	1	119	119
		400	1	90	90
		600	1	119	119
		TOTAL	**3**	**90- 119**	**109 ± 17**
Cleaned wheat grain	Malathion	0.01	1	111	111
		1.0	1	98	98
		16.0	1	101	101
		TOTAL	**3**	**98- 111**	**103 ± 7**
	Malaoxon	0.01	1	98	98
		1.0	1	98	98
		TOTAL	**2**	**98**	**98**
	Desmethyl malathion	0.01	1	71	71
		1.0	1	71	71
		TOTAL	**2**	**71**	**71**
Wheat bran	Malathion	0.01	1	101	101
		1.0	1	102	102
		20.0	1	103	103
		TOTAL	**3**	**101- 103**	**102 ± 1**
	Malaoxon	0.01	1	106	106
		1.0	1	102	102
		TOTAL	**2**	**102-106**	**104**

TABLE C.1. Summary of Concurrent Recoveries of Malathion from Wheat Grain

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev (%)
	Desmethyl malathion	0.01	1	80	80
		1.0	1	80	80
		TOTAL	**2**	**80**	**80**
Wheat germ	Malathion	0.01	1	94	111
		20.0	1	104	104
		TOTAL	**2**	**94- 104**	**99**
	Malaoxon	0.01	1	95	95
		1.0	1	103	103
		TOTAL	**2**	**95- 103**	**99**
	Desmethyl malathion	0.01	1	74	74
		1.0	1	79	79
		TOTAL	**2**	**74- 79**	**76**
Wheat straight flour	Malathion	0.01	1	110	110
		5.0	1	101	101
		TOTAL	**2**	**101- 110**	**106**
	Malaoxon	0.01	1	98	98
		1.0	1	100	100
		TOTAL	**2**	**98- 100**	**99**
	Desmethyl malathion	0.01	1	99	99
		1.0	1	83	83
		TOTAL	**2**	**83- 99**	**91**
Wheat middlings	Malathion	0.01	1	96	96
		1.0	1	106	106
		5.0	1	95	95
		TOTAL	**3**	**95- 106**	**99 ± 6**
	Malaoxon	0.01	1	99	99
		1.0	1	101	101
		TOTAL	**2**	**99- 101**	**100**
	Desmethyl malathion	0.01	1	113	113
		1.0	1	90	90
		TOTAL	**2**	**90- 113**	**102**
Wheat shorts	Malathion	0.01	1	104	104
		20.0	1	92	92
		TOTAL	**2**	**92- 104**	**98**
	Malaoxon	0.01	1	99	99
		1.0	1	104	104
		TOTAL	**2**	**99- 104**	**102**
	Desmethyl malathion	0.01	1	86	86
		1.0	1	91	91
		TOTAL	**2**	**86- 91**	**88**
Wheat whole meal flour	Malathion	0.01	1	109	109
		1.0	1	101	101
		20.0	1	101	101
		TOTAL	**3**	**101- 109**	**104 ± 5**
	Malaoxon	0.01	1	110	110
		1.0	1	104	104
		TOTAL	**2**	**104- 110**	**107**
	Desmethyl	0.01	1	76	76

TABLE C.1. Summary of Concurrent Recoveries of Malathion from Wheat Grain

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev (%)
	malathion	1.0	1	83	83
		TOTAL	**2**	**76- 83**	**80**
Wheat 550 flour	Malathion	0.01	1	102	102
		5.0	1	104	104
		TOTAL	**2**	**102- 104**	**103**
	Malaoxon	0.01	1	102	102
		1.0	1	104	104
		TOTAL	**2**	**102- 104**	**103**
	Desmethyl malathion	0.01	1	89	89
		1.0	1	96	96
		TOTAL	**2**	**89- 96**	**92**
Wheat vital gluten	Malathion	0.06	1	118	118
		1.0	1	106	106
		TOTAL	**2**	**106- 118**	**112**
	Malaoxon	0.01	1	106	106
		1.0	1	104	104
		TOTAL	**2**	**104- 106**	**105**
	Desmethyl malathion	0.01	1	86	86
		1.0	1	85	85
		TOTAL	**2**	**85- 86**	**86**
Wheat whole meal bread	Malathion	0.01	1	103	103
		1.0	1	97	97
		5.0	1	102	102
		TOTAL	**3**	**97- 103**	**101 ± 3**
	Malaoxon	0.01	1	111	111
		1.0	1	97	97
		TOTAL	**2**	**97-111**	**104**
	Desmethyl malathion	0.01	1	79	79
		1.0	1	67	67
		TOTAL	**2**	**67- 79**	**73**
Wheat white bread	Malathion	0.01	1	97	97
		1.0	1	97	97
		TOTAL	**2**	**97**	**97**
	Malaoxon	0.01	1	105	105
		1.0	1	94	94
		TOTAL	**2**	**97- 105**	**100**
	Desmethyl malathion	0.01	1	75	75
		1.0	1	88	88
		TOTAL	**2**	**75- 88**	**82**

TABLE C.2. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration (days)	Interval of Demonstrated Storage Stability
Desmethyl Malathion			
Wheat grain	-20±5	104	Present study

Malathion and Malaoxon			

TABLE C.3. Residue Data from Wheat Grain.

Sampling Event	Trt ID	Sample amount (lbs)	Malathion (ppm)		Malaoxon (ppm)		Desmethyl Malathion (ppm)	
			Sample	Mean	Sample	Mean	Sample	Mean
Prior to any applications	UTC	2.2	<0.01		ND		ND	
Post-Appl#2 Pre-Appl#3	TRT#2-A	2.2	5.17	6.23	<0.01	<0.01	0.240	0.263
	TRT#2-A	3.55	7.28		<0.01		0.286	
	TRT#2-B	3.35	8.45	7.56	<0.01	<0.01	0.515	0.421
	TRT#2-B	3.55	6.66		<0.01		0.327	
	TRT#2-C	3.55	9.28	8.74	<0.01	<0.01	0.584	0.449
	TRT#2-C	3.8	8.19		<0.01		0.313	
Post-Appl#3	TRT#2-A	4.15	9.73	11.1	<0.01	<0.01	0.490	0.522
	TRT#2-A	3.65	12.4		<0.01		0.554	
	TRT#2-B	3.45	9.12	9.04	<0.01	<0.01	0.380	0.368
	TRT#2-B	3.75	8.96		<0.01		0.356	
	TRT#2-C	3.55	8.90	9.20	<0.01	<0.01	0.254	0.382
	TRT#2-C	3.15	9.50		<0.01		0.510	
Pre-Appl#4	TRT#2-A	2.8	7.04	8.21	<0.01	<0.01	0.287	0.337
	TRT#2-A	2.3	9.38		<0.01		0.386	
	TRT#2-B	2.8	7.68	8.72	<0.01	<0.01	0.306	0.297
	TRT#2-B	2.45	9.76		<0.01		0.287	
	TRT#2-C	2.45	6.69	8.02	<0.01	<0.01	0.258	0.313
	TRT#2-C	2.2	9.34		<0.01		0.368	
Post-Appl#4	TRT#2-A	2.7	12.3	9.85	<0.01	<0.01	0.485	0.408
	TRT#2-A	2.65	7.39		<0.01		0.330	
	TRT#2-B	2.5	10.0	10.1	<0.01	<0.01	0.377	0.382
	TRT#2-B	2.5	10.2		<0.01		0.387	
	TRT#2-C	2.75	10.3	10.1	<0.01	<0.01	0.397	0.380
	TRT#2-C	2.7	9.79		<0.01		0.362	
10 Days Post-Appl#4	TRT#2-A	2.55	13.4	13.4	<0.01	<0.01	0.613	0.617
	TRT#2-A	2.4	13.4		<0.01		0.621	
	TRT#2-B	2.3	13.6	12.9	<0.01	<0.01	0.698	0.632
	TRT#2-B	2.75	12.1		<0.01		0.565	
	TRT#2-C	2.8	9.36	10.4	<0.01	<0.01	0.442	0.476

TABLE C.3. Residue Data from Wheat Grain.

Sampling Event	Trt ID	Sample amount (lbs)	Malathion (ppm)		Malaoxon (ppm)		Desmethyl Malathion (ppm)	
			Sample	Mean	Sample	Mean	Sample	Mean
	TRT#2-C	2.65	11.4		<0.01		0.509	
29 Days Post-Appl#4	UTC	2.7	0.104[1]		ND		<0.01	
	TRT#2-A	3.0	15.1	12.9	<0.01	<0.01	0.662	0.562
	TRT#2-A	2.75	10.7		<0.01		0.461	
	TRT#2-B	2.55	15.0	13.9	<0.01	<0.01	0.669	0.620
	TRT#2-B	2.45	12.7		<0.01		0.570	
	TRT#2-C	2.2	10.6	11.7	<0.01	<0.01	0.446	0.525
	TRT#2-C	2.4	12.7		<0.01		0.603	

UTC- untreated control; SD- standard deviation; ND- not detected
[1]The source of these residues in the control samples is not known, but it is believed to have occurred either during the field phase and/or the processing phase and not the analytical phase.

TABLE C.4. Processed Commodity Sample Residues

Field Sample[1]	Trt ID	Sample Type	Malathion ppm	Malaoxon ppm	Desmethyl Malathion ppm
Processing Bulk Sample	UTC[2]	Pre-Processing Grain	<0.01	ND	ND
		Aspirated Grain Fractions	0.387	<0.01	0.0720
		Cleaned Grain	<0.01	ND	ND
		Bran	<0.01	ND	ND
		Germ	0.0311	ND	ND
		Straight Flour	<0.01	ND	ND
		Middlings	<0.01	ND	ND
		Shorts	<0.01	ND	ND
		Whole Meal Flour	<0.01	ND	ND
		550 Flour	<0.01	ND	ND
		Vital Gluten	0.0155	ND	ND
		Whole Meal Bread	<0.01	ND	ND
		White Bread	<0.01	ND	ND
Processing Bulk Sample	TRT#2	Pre-Processing Grain	15.0	<0.01 (0.0046)	0.610
		Aspirated Grain Fractions	2690	0.984	502
		Cleaned Grain	11.9	<0.01 (0.0044)	0.244
		Bran	8.08	<0.01 (0.0016)	0.116
		Germ	14.0	<0.01 (0.0039)	0.0936
		Straight Flour	1.34	ND	0.0122

		Middlings	3.26	<0.01 (0.0010)	0.0406
		Shorts	9.04	<0.01 (0.00136)	0.0626
		Whole Meal Flour	11.2	<0.01 (0.0045)	0.232
		550 Flour	2.14	ND	0.0302
		Vital Gluten	0.0178	ND	ND
		Whole Meal Bread	1.84	<0.01 (0.0010)	0.346
		White Bread	0.295	<0.01 (0.0004)	0.0662

[1] Sample number prefaced by the study number AA070707.
[2]The source of these residues in the control samples is not known, but it is believed to have occurred either during the field phase and/or the processing phase and not the analytical phase.
[3] UTC- untreated control; ND- not detected
[4] Values shown in parentheses were <LOQ

TABLE C.5. Residue Concentration from Pre-Processing Grain to Processed Commodities

From	To	Malathion	Malaoxon	Desmethyl Malathion
Pre-Processing Grain	**Aspirated Grain Fractions**	179	214	823
	Cleaned Grain	0.79	0.95	0.40
	Bran	0.54	0.35	0.19
	Germ	0.93	0.84	0.15
	Straight Flour	0.09	0.00	0.02
	Middlings	0.22	0.23	0.07
	Shorts	0.60	0.30	0.10
	Whole Meal Flour	0.75	0.99	0.38
	550 Flour	0.14	0.00	0.05
	Vital Gluten	0.00	0.00	0.00
	Whole Meal Bread	0.12	0.22	0.57
	White Bread	0.02	0.09	0.11

* Concentration Factor = Processed Commodity Residue / Pre-Processing Grain Residue (e.g. germ= germ treated 14/ 15 pre-processing grain=0.93)
If the concentration factor is >1 then residues increased during processing, if it is <1 then residues declined during processing

D. CONCLUSION

Stored wheat was conducted to determine the magnitude of malathion, malaoxon, and desmethyl malahtion residues in wheat grain and wheat processed commodities. The empty storage bins were treated with a malathion emulsifiable concentrate formulation containing 57% malathion prior to loading of the grain, and the grain was subsequently treated three times with a malathion dust formulation. Samples were taken immediately before and after application and 10 and 29 days after the last application. Quantifiable residues of malathion and desmethyl malathion were detected in whole grain and wheat processed commodities. Malaoxon was found at levels <LOQ in any wheat grain samples or processed commodities. The sample storage intervals and conditions are supported by the available storage stability data.

E. REFERENCES

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F. DOCUMENT TRACKING

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